Chemistry 125 First Examination Answers **September 21, 2005**

Average Score: 77.7 1/3 of scores greater than 84. 2/3 of scores greater than 73

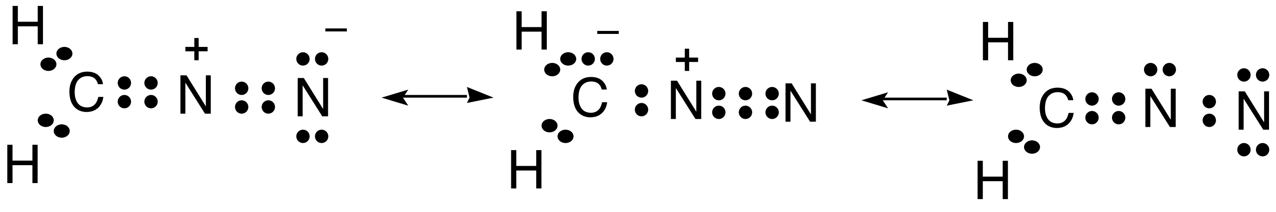
Read each question carefully to see what it asks for (bold face is used to help highlight questions).
Make sure you are answering the question, not just saying something vaguely relevant to its topic.

1. (7.5 minutes).

A) Add dots to the following diagrams to complete **two reasonable Lewis structures** for H_2CNN.

B) Show their relationship by drawing the appropriate **arrow symbol** in the box **between** your two structures.

C) Mention **a strength and a weakness** for **each** way of drawing the structure (2 strengths, 2 weaknesses).



Strengths:	Complete Octets Negative Charge on N	Complete Octets	No Charge Separation
Weaknesses:	Charge Separation	Charge Separation Negative Charge on C	Incomplete Octet on one N

2. (5 min) Choose a scientific discovery that occurred within 75 years of the founding of Yale College and is relevant to the subject matter of the course thus far. **Describe** in a sentence or two the experiment on which the discovery was based and **name** the discoverer.

The most popular correct choices within 75 years of Yale's founding in 1703 were:

Newton's "Experimentum Crucis" (~1670) showing that refraction of red light by a second prism did not cause it's color to vary ("nec variat lux fracta colorem"). Thus light behaved more like a substance with characteristic properties than like a train of pulses created during refraction (Hooke's idea).

Hooke's determination of Hooke's Law (~1678) showing that the extension of a spring was proportional to the weight it supported ("ut tensio sic vis")

Franklin's observation that ripples over an enormous area of water (half an acre) were stilled by a teaspoonful of oil, showing that an invisibly thin layer could be detected by its macroscopic effect. Although he did not make the calculation, the thickness of the monomolecular layer was about 2 nm.

Answers involving x-rays or electrons, discovered at the end of the 1800s, were obviously out of bounds.

3. (3 minutes) Give approximate values for the following (with units):

A) the diameter of a human hair: 50-100 μm

B) the width of the tip of an AFM probe where it touches the sample: 20 nm

C) the diameter of an atomic nucleus: 10 fm

4. (3 minutes) For one-dimensional quantum mechanics

A) **Name** a potential for which all energies are quantized: Harmonic Oscillator (Hooke's Law)

B) **Name** a potential for which no energies are quantized: Constant (or Decaying Exponential)

C) **Name** a potential for which some energies are quantized, and some non-quantized: Morse

5. (6 minutes) **Explain** how it is that STM can show ***individual*** molecules, but not bonds, while X-ray diffraction can show bonds, but not ***individual*** molecules.

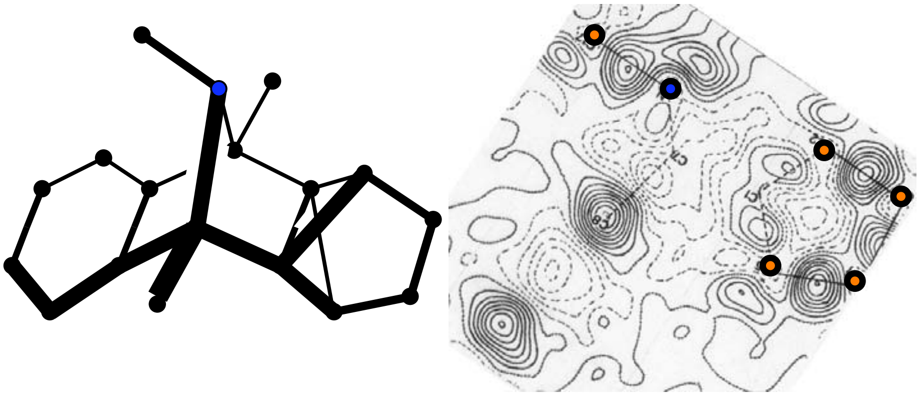
STM uses electrical conductivity from a single atom at the end of a sharp needle to detect proximity to atoms in the sample substance (held on a conductive surface). Although it can “feel” an individual molelcules, and indeed individual atoms of that molecule, the tip is a single atom, it is **too wide** to detect variations in electron density on a sub-atomic scale. (The sensitivity is probably also inadequate to detect the small variation in electron density that results from bonding.)

X-ray diffraction from a single molecule is far too weak to detect. Detectable diffraction results from **cooperative scattering by many molecules**, preferably in a crystal, where the 3D periodicity of the lattice gives strong intensity at specific points in “reciprocal space”. Since scattering comes from many molecules, one does not “see” individual molecules, but rather the **average electron density distribution about an average molecule.** One can measure this average density with **great precision**, however, so that it is meaningful to subtract the calculated electron density of independent spherical atoms to visualize how atomic density changes in forming bonds. (Note that although the positions of atomic nuclei are not directly observed by x-ray diffraction, these positions are easily inferred with great precision from the centers of highest electron density.)

6. (3.5 minutes) What is reciprocal about the “reciprocal space” of x-ray diffraction photographs?

X-ray photographs show the angles at which an x-ray beam has been bent by passing through a sample. When scattering centers are close together, the beam must be scattered at a high angle to achieve reinforcement of waves that differ in path length by a single wavelength. When the scattering centers are far apart, a more modest deflection suffices to give a single-wavelength path difference. Thus close spacing gives high angles, and distant spacing gives low angles, in a “reciprocal” relationship.

7. (5 minutes) Discuss a bonding curiosity in **ONE** of these two difference density maps. **(Don’t do both)**



The most curious feature in this map is the absence of bonding density at the “missing” corner of the pentagon on the right. The map shows many contours for all other bonds (C-H and C-C) that lie within or intersect the medial plane of the molecule, and it even shows the expected lone pair on N, but there is no sight of the bond joining the two carbons that are involved in two three-membered rings each. (We did not explain this invisibility, saying only that it was a curiosity crying out for theoretical rationalization – coming soon.)

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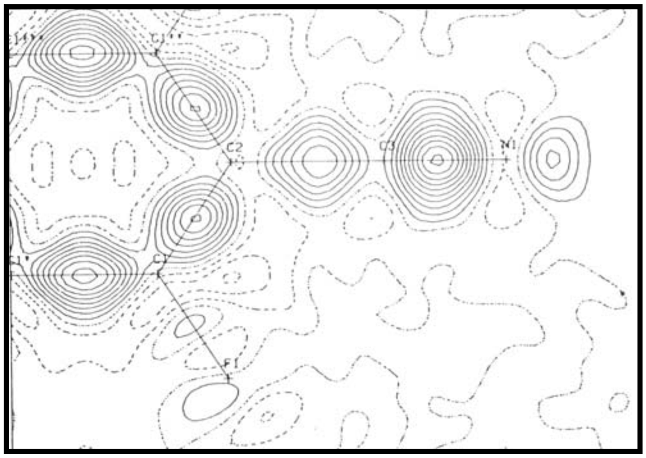


The curiosity in this map is the absence of bonding electron density in the C-F bond in the lower left quadrant. Dunitz explains this anomaly by pointing out that it cannot be correct to subtract a spherically averaged F atom from the observed electron density, since, without any bonding shift this would require an impossible amount of electron density between C and F (11/4 of an electron, where the maximum is 2). If one subtracted a F atom with only one electron in the bond-forming region, the bond would re-emerge.

(It is true that this compound also showed a curiously round cross-section of the C-N triple bond, but the cross section is not shown in this map. That region in this map would look round whatever the shape of the cross section perpendicular to the plane of the map. The same is true of the cross-section of bonds in the aromatic ring. The unshared pair on the N atom is not sufficieny unexpected to qualify “as a bonding curiosity.” The equality of bonds in the phenyl ring is curious if you believe in individual Kekulé structure of benzene, but we are getting beyond that naiveté.)

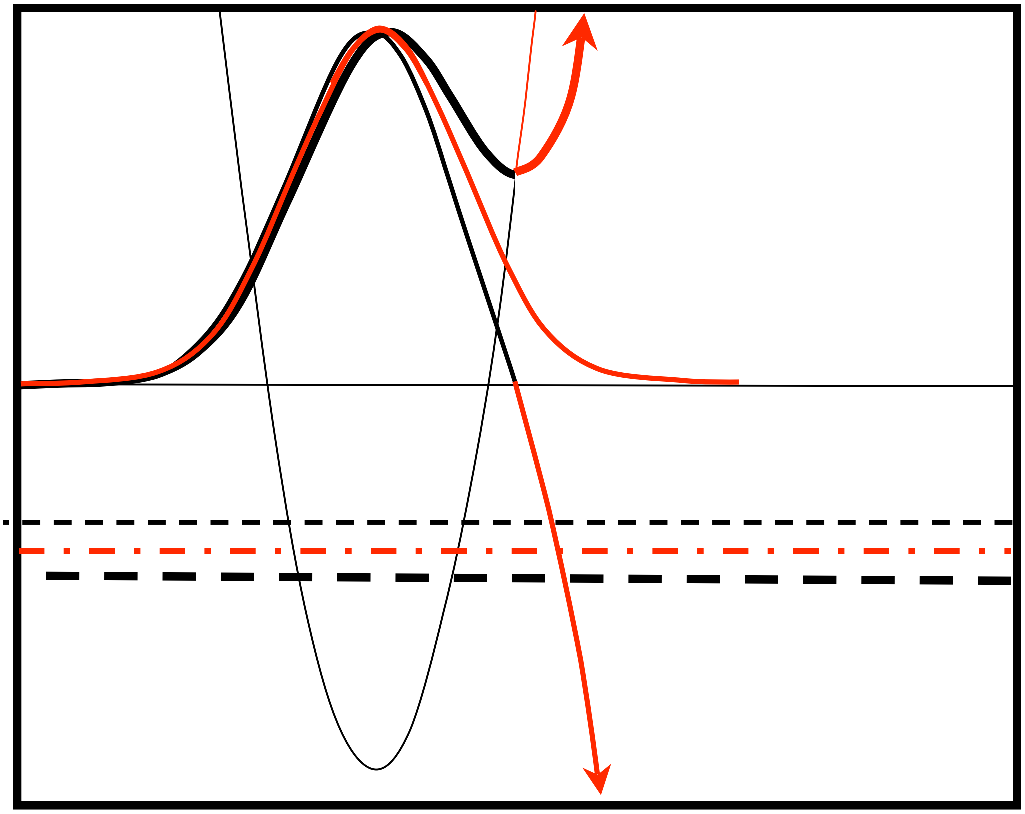
8. (5 minutes) **Explain** why wave functions for the “1-dimensional atom” (Coulombic potential) are decaying exponentials far from the nucleus.

For such an inverse potential (1/r) the potential energy approaches zero, and thus ceases to change appreciably, as one gets far from the nucleus. Thus the difference between total and potential energy also becomes effectively constant. When the electron is bound to the nucleus (total energy less than that for a free electron), the kinetic energy is a negative constant, for which we showed that the exponential is a solution to Schrödinger’s equation. It must be a decaying (rather than exploding) exponential to avoid divergence to infinity.

(Note that many answers failed to note that the kinetic energy becomes a negative CONSTANT, which gives an exponential solution. These answers typically used the word “exponential” loosely to mean approaching $\Psi=0$ asymptotically. The best answer is much more definite and elegant.)

9. (12 min) The two figures below are incomplete. The three **straight** lines (denoting Ψ=0 and two trial total energies) are complete, but only the left half of the three **curves** denoting two trial wave functions and the potential energy are shown. It is possible to complete these three curves in two different ways (corresponding to a single minimum and a double minimum) and to draw another Ψ and energy so as to explain the source of bonding.
Complete the single-minimum and double-minimum **figures,** and use a few words to **show how they explain bonding.**

Completing the diagram (in red) as an harmonic (Hooke's Law) **single-minimum** potential shows the existence of a satisfactory nodeless wave function with an **energy between** those of the trial functions that had too low an energy (and thus diverged to + infinity) and too high an energy (and thus diverged to – infinity).



Completing the diagram (in red) as a **double minimum** composed of two harmonic single-minima, each like the one in the previous figure, shows that the original black curves are in fact **satisfactory** wave functions with the energies shown.

Thus when two single minima "come together" to form a double minimum, two new wave functions are generated: one **bonding** function with no new nodes, increased probability density at the midpoint, and a lower energy that the single-minimum function; and one **antibonding** function with an extra node, zero probability density at the midpoint, and higher energy that that for the single minimum.